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COMPARISON OF A MODIFIED KJELDAHL
AND VACUUM FUSION TECHNIQUES
FOR DETERMINATION OF NITROGEN
IN TANTALUM ALLOYS

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COMPARISON OF A MODIFIED KJELDAHL AND VACUUM FUSION TECHNIQUES FOR DETERMINATION OF NITROGEN IN TANTALUM ALLOYS

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SUMMARY

This report compares results obtained for the determination of nitrogen in the tantalum alloys T-111 (Ta-8W-2Hf) and T-222 (Ta-10W-2.5Hf-0.1C) by Kjeldahl and vacuum fusion procedures.

The Kjeldahl method used consists of rapid dissolution of a 1- to 2-gram solid metal sample in a hydrofluoric-, phosphoric-, chromic-acid mixture, addition of excess caustic, and distillation of ammonia into dilute boric acid using argon as a flushing gas. The very sensitive nitroprusside-catalyzed indophenol reaction is used for colorimetric measurement. The blank amounts to 8 to 10 micrograms nitrogen, of which a significant portion is believed to arise from the laboratory atmosphere.

The vacuum fusion technique is based on the melting of the metal sample in a graphite crucible in vacuum and collecting, separating, and measuring the evolved gases. The tantalum alloys T-111 and T-222 may be successfully analyzed using a 0.5- to 1.0-gram solid sample with a platinum-tin bath, platinum flux technique, an extraction time of 20 minutes, and temperature of approximately 2000^o C. The vacuum fusion blank ranged from 0.7 to 0.9 microgram nitrogen.

Results are shown by each technique for the determination of nitrogen in T-111 and T-222. Analyses were repeated on several different days by each technique. In the 5- to 25-ppm range, the relative standard deviation was 3 to 9 percent by the Kjeldahl procedure and 4 to 8 percent by vacuum fusion.

The agreement of the nitrogen results by the two techniques is considered satisfactory and tends to increase confidence that the vacuum fusion results for nitrogen in the tantalum alloys are valid under these conditions. Previously, no precision data for comparison of the analysis of tantalum for low levels of nitrogen by vacuum fusion and other methods have been published.

INTRODUCTION

The refractory alloys T-111 and T-222 are promising candidates for structural use in a space-power reactor. The interstitial elements carbon, hydrogen, oxygen, and nitrogen are critical to the strength and corrosion resistance of refractory metals at high temperature. Thus, it is important to monitor changes in nitrogen content and to determine nitrogen in these metals and alloys in the low ppm range. The usual range of nitrogen in molybdenum and tungsten is well below 5 ppm, but in niobium and tantalum it may be 10 to 50 ppm or higher.

Low contents of nitrogen in metals have been determined either by vacuum fusion techniques or by variations of the Kjeldahl procedure. The vacuum fusion method consists of melting a metal sample in a graphite crucible in vacuum and collecting, separating, and measuring the evolved gases. In the Kjeldahl method, the sample is decomposed in acid, and the nitrogen fixed as ammonium ion. The nitrogen is then determined by boiling the sample with sodium hydroxide and absorbing the evolved ammonia in dilute acid. The ammonia can then be determined by titrimetry or colorimetry.

There has only been a limited amount of work done on the refractory metals showing a comparison of results obtained for nitrogen in the same material by the two methods. Where comparisons have been made, results by vacuum fusion are generally low (refs. 1 and 2) compared with results by the Kjeldahl method. The vacuum fusion method, however, appears to be more sensitive (the blank is 0.5 to 1.0 $\mu\text{g N}$) and thus better suited to the determination of nitrogen at the lowest levels in those metals which release all their nitrogen with a platinum bath.

This report evaluates the vacuum fusion method, as compared with a modified Kjeldahl method, for the determination of nitrogen in tantalum alloys. Vacuum fusion has many advantages, but, because the quantitative release of nitrogen from different metals is not always obtained under a given set of conditions, it is necessary to use the chemical Kjeldahl method for reference. However, the Kjeldahl method has been limited by a higher blank and a lower sensitivity. Recent developments have improved the Kjeldahl method in both respects, so it should now be possible to evaluate nitrogen determinations at low levels in the refractory metals niobium, tantalum, molybdenum, and tungsten.

The section VACUUM FUSION METHOD summarizes the conditions used and the results obtained when three samples of T-111 and one sample of T-222 were analyzed for nitrogen. The section KJELDAHL PROCEDURE describes several modifications to the standard apparatus and procedure. The same samples that were analyzed by the vacuum fusion procedure were analyzed by the modified Kjeldahl apparatus and procedure. The chemical dissolution procedure used was developed by Kallmann et al.

(ref. 3). The distillation procedure was adapted from one described by Ciaranello (ref. 4). The indophenol reaction was used for measurement of ammonia (refs. 5 to 11). The spectrophotometric procedure used was previously described by Mann (ref. 10). The method used to monitor ammonia in the laboratory atmosphere is similar to that of Leithe and Petschl (ref. 12).

VACUUM FUSION METHOD

The vacuum fusion method has been used for many years to determine gases in metals. The greatest emphasis has been on the determination of oxygen. Values for nitrogen are normally obtained along with oxygen. Nitrogen values are considered less accurate than those for oxygen in metals such as niobium, tantalum, molybdenum, and tungsten (ref. 13). The lack of confidence has been fostered by the inability of vacuum fusion to yield nitrogen values that agree with the chemical Kjeldahl method. There has been a general belief that low nitrogen values indicate incomplete extraction. The Kjeldahl method usually gives higher values for nitrogen than the vacuum fusion method. For this reason, the Kjeldahl method has been the preferred method for determining nitrogen in refractory metals.

Goward, however, in his review of the status of vacuum fusion analysis for nitrogen in metals, stated his belief that the platinum bath vacuum fusion technique would eventually prove successful for the refractory metals (ref. 1). In an article on the determination of nitrogen using carrier gas fusion, Dallmann and Fassel cited a few vacuum fusion results for nitrogen in refractory metals, but no comparison of precision was shown between Kjeldahl and vacuum fusion results (ref. 14).

In a recent report on the Kjeldahl method, Kallmann and co-workers stated that nitrogenous impurities in reagents could be reduced to ammonia during sample dissolution (ref. 3). This reduction does not occur in the blank because of the absence of oxidizable sample metal. Kallmann proposed a method in which a high concentration of stable oxidant was maintained during sample dissolution. When Kallmann's method was used to determine nitrogen in the niobium alloy FS-85, good agreement was shown with results obtained by the platinum bath vacuum fusion method (ref. 15).

In our laboratory, oxygen has been determined in niobium, tantalum, and their alloys using the platinum-tin bath, platinum flux vacuum fusion method. When a nitrogen determination was required, a separate Kjeldahl analysis was performed. The possible savings in materials and time plus the advantages of obtaining both nitrogen and oxygen on the same sample prompted a reappraisal of the vacuum fusion nitrogen determination.

KJELDAHL PROCEDURE

At the present time, the method most often used for the determination of nitrogen is a modified Kjeldahl procedure. It is applicable to all metals and is usually regarded as more reliable and precise than vacuum fusion (ref. 16). At low concentrations (i. e., 0 to 100 ppm), a spectrophotometric measurement is now used instead of the titrimetric finish used for higher amounts. In the second case, ammonium borate is titrated to boric acid with 0.007 normal standard acid (1 ml \equiv 0.1 mg N) using the color change of the mixed indicator methyl purple to find the equivalence point. Formerly, Nessler's reagent was used (ref. 17), first visually and later colorimetrically, to measure the ammonia nitrogen in the Kjeldahl distillate. Recently, the advantages of the indophenol spectrophotometric method have won it wide popularity.

There are several sources of ammonia nitrogen that cause high blanks in the Kjeldahl determination. These include chemical reagents, laboratory air, and the preparation of the sample surface. Sulfuric acid and hydrogen peroxide are known to contain traces of ammonium ion (NH_4^+). Other reagents contain traces of nitrate ion (NO_3^-), which does not affect the blank but may be reduced by metal to NH_4^+ and thus cause high nitrogen results for the sample. Potassium dichromate is a stable oxidant: It does not coat the sample with insoluble products and does not oxidize NH_4^+ to free nitrogen. Since dichromate ion is present in large excess, there is little chance for reduction of NO_3^- by the sample (ref. 3).

There is also ammonia present in the laboratory air. For this reason, it is frequently recommended that nitrogen determinations be made in a location isolated from the main chemical laboratory. In our chemical laboratory, the air usually contains 5 to 6 micrograms ammonia nitrogen per cubic meter of air when samples are being analyzed for nitrogen and no ammonia is being used in the immediate area. The laboratory air is believed to be a major source of nitrogen contamination. In our procedure, ammonia is absorbed in dilute boric acid (ref. 18) instead of dilute sulfuric acid but otherwise the procedure for measuring ammonia in air is similar to that of Leithe and Petschl (ref. 12).

The preliminary surface treatment of the sample is another possible source of contamination. Prior to analysis, samples are commonly filed or chemically etched (or both). Very small or irregular samples are more easily etched than filed. The best sample form is the one with the least exposed surface. In the work reported here, all samples were etched with acid before both Kjeldahl and vacuum fusion analysis. The chemical dissolution of metal samples by Kallmann's procedure greatly reduces exposure to atmospheric contamination. Samples are usually dissolved in less than 2 hours. Using loosely stoppered bottles, samples are dissolved without addition of more acid and exposure to laboratory air is further minimized.

Chemical reagents may often be purified to remove traces of impurities. The ammonia-free water (refs. 11 and 19) used here is distilled and then passed through two mixed-bed demineralizer columns, the last pass just before use. The 50-percent caustic solution is boiled in a stainless-steel Teflon-lined beaker for 15 to 20 minutes, then quickly cooled and stored in a plastic bottle. Phosphoric acid may be purified of ammonia by heating five parts with one part perchloric acid until fuming ceases. Potassium chromate may be purified by evaporating a solution of 700 grams in 1 liter of water in the presence of 3 grams of potassium hydroxide, followed by gradual heating to 500° C in a muffle furnace (ref. 20). Purification of our reagents had only a slight effect on the blank. The size and variation of the blank in the Kjeldahl method has previously made unreliable the determination of less than 25 ppm nitrogen. In our laboratory, the blank usually amounts to 8 to 10 micrograms nitrogen, of which a major part is attributed to atmospheric contamination.

The present paper described several modifications of the Kjeldahl apparatus and procedure for the determination of nitrogen in the tantalum-base alloys T-111 and T-222. The modified method has advantages over similar ones commonly used.

The first modification to the apparatus (see fig. 1) was to use a larger distillation flask (300 ml) in order to accommodate the large amount of salts formed by the addition

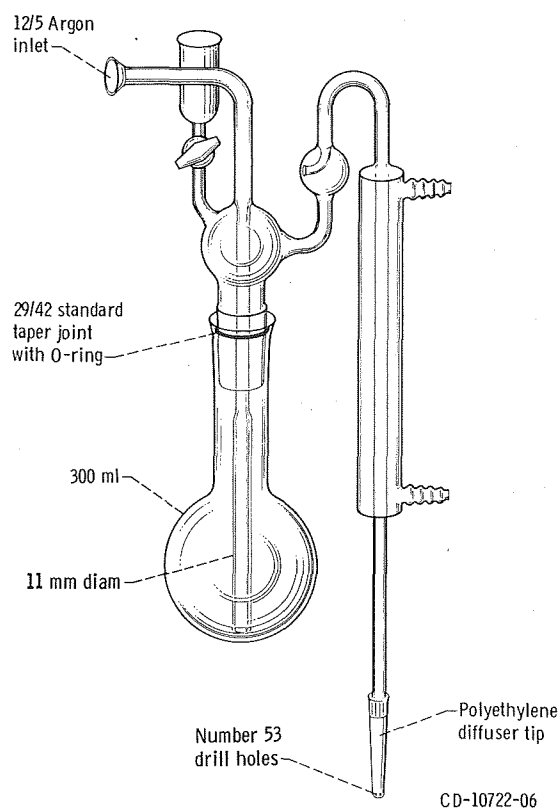


Figure 1. - Kjeldahl distillation apparatus.

of excess caustic to hydrofluoric-phosphoric-chromic acid solutions of refractory metals. The round-bottom distillation flask has an outer 29/42 standard taper joint and is sealed with an ethylene-propylene O-ring on the inner joint. This prevents the joint from "freezing" and permits easy disassembly for cleaning after contact with caustic solutions. The diameter of the bottom 12 centimeters of the gas inlet tube was increased from 8 to 11 millimeters in order to prevent salts from clogging the tube during the distillation. The rest of the distillation apparatus is standard as may be seen from the figure.

The next modification from common Kjeldahl practice is the use of an inert carrier gas and direct heating of the distillation flask instead of the usual flow of steam. This change makes the manipulations easier and faster. With this system, it is unnecessary to heat a large volume of water to generate steam, and the inert gas flow is easily regulated so that there is no chance of a sudden pressure decrease with resultant loss of sample. Also, it is possible to run two or more distillation systems simultaneously using a separate inert gas cylinder for each system to avoid pressure fluctuations.

Recent developments have considerably increased the sensitivity of the colorimetric measurement. The intense blue indophenol color given by the reaction of ammonia with phenol and hypochlorite originated with Berthelot in 1859 (ref. 21). The sensitivity of the indophenol procedure can be further increased by the presence of various catalysts. Iron, chromium, and manganese accelerate the reaction, but copper and oxidants such as persulfate inhibit it (ref. 8). The catalyzed indophenol reaction is more sensitive than that of ammonia with thymol and hypochlorite (refs. 11 and 22), and it is also about 10 times more sensitive than the Nessler reaction (refs. 17 and 19), which has the disadvantages that the reaction product is colloidal and the blank value is large and variable.

Chaney and Marbach (ref. 5) were the first to recommend the use of sodium nitroprusside as catalyst. This reagent not only accelerates the speed of the reaction but also increases to a maximum the conversion of ammonia to indophenol. The procedure described here is similar to one recommended by Mann (ref. 10). In this report, 1 microgram of ammonia nitrogen in a 100-milliliter volume gives an optical density of 0.016 absorbance units when measured in a 1-centimeter cell at 630 nanometers. This is equivalent to a molar absorption coefficient of 22 400 and is exactly the same sensitivity reported by Bach et al. (ref. 6) using a slightly different indophenol procedure. Several Japanese investigators (refs. 22 and 23) have further increased the sensitivity of the indophenol procedure by using organic solvent extraction.

The principal advantage of high sensitivity is that relatively small samples of solid material are sufficient for determination of low nitrogen content. Such small samples

TABLE I. - COMPARISON OF RESULTS FOR DETERMINATION OF NITROGEN IN
T-111 AND T-222 BY KJEDAHN AND VACUUM FUSION METHODS

Sample	Rod diameter		Source	Alloy	Kjedahl method					Vacuum fusion method				
	in.	cm			Nitrogen, ppm	Average, ppm	Standard deviation, ppm	Relative standard deviation, percent	Blank, μg	Nitrogen, ppm	Average, ppm	Standard deviation, ppm	Relative standard deviation, percent	Blank, μg
1	1/4	0.635	Materials Advisory Board	T-111	8.7 7.9 7.7 8.4 8.1 8.1 8.7	8.2	0.4	4.9	10.8	10.0 9.0 9.6 9.9 9.5 9.8 9.9 10.3 10.1 9.2	9.7	0.4	4.1	0.7 - 0.9
2	1/2	1.27	Commercial	T-111	7.7 6.9 7.4 7.3 7.0 6.8 7.5	7.2	0.4	5.6	7.5	7.6 7.9 6.9 7.0 6.4 7.2 7.1 6.6 7.4 8.3	7.2	0.6	8.3	0.7 - 0.9
3	3/4	1.905	Commercial	T-111	9.4 9.7 9.4 9.3 9.6 8.7 9.4 9.2 9.1 9.0 9.8 9.2 9.3	9.3	0.3	3.2	8.4	9.4 10.2 9.0 9.6 9.9 10.5 10.0 9.8 8.7 9.4	9.6	0.5	5.2	0.7 - 0.9
4	3/4	1.905	Commercial	T-222	20.9 24.2 23.9 20.6 22.6 24.9 28.7 23.1 25.0 24.7 21.9 22.5 22.2 25.3	23.6	2.1	8.9	8.4	21.3 21.9 22.2 22.2 21.0 21.6 22.6 22.5 24.8 24.8	22.5	1.3	5.8	0.7 - 0.8

may now be dissolved rapidly with a minimum of atmospheric contamination permitting determination of less than 25 ppm nitrogen with a higher degree of precision than was formerly possible.

DISCUSSION OF RESULTS

The data reported in table I indicate that equivalent results for the determination of nitrogen in the tantalum alloys T-111 and T-222 are obtained by the vacuum fusion and Kjeldahl techniques. The precision of the vacuum fusion results is not significantly different from the precision of the Kjeldahl results in spite of the much larger blank of the Kjeldahl method.

In the case of the Kjeldahl results, samples 1 and 2 were analyzed on one day, sample 3 was analyzed on two days, and sample 4 was analyzed on three days. Each Kjeldahl blank reported is the average of two or more values. The blank included the same amounts of reagents and underwent treatment identical to that of the samples. For the vacuum fusion results, samples 1 and 2 were analyzed on three days and samples 3 and 4 were analyzed on four days. A single vacuum fusion blank was run on each day samples were analyzed.

The T-111 from the Material Advisory Board (MAB) (sample 1) was included among the samples analyzed because it is supposed to be a uniform reference material. It has been available from the National Bureau of Standards since 1965 and has been analyzed by many laboratories interested in the determination of traces of carbon, nitrogen, oxygen, and hydrogen in refractory metal alloys (ref. 24).

For comparison with the results reported here, Chase (ref. 25) in 1965 reported, round-robin results for nitrogen in MAB T-111 alloy by 12 participating laboratories using the Kjeldahl procedure:

	Round-robin 1	Round-robin 2
Average N, ppm	31	20
Standard deviation, ppm	41	9
Relative standard deviation, percent	132	45
Range, ppm	2 - 162	11 - 38

The blank values ranged from 0 to 30 micrograms. The cooperating laboratories experienced great difficulty with this determination because a method for dissolving solid pieces of material in a reasonable period of time was not then available. Ground rules for the round-robins specified use of 1-gram, solid, undivided samples prepared by filing and then rinsing in a residue-free solvent. All analyses were performed three times, once each on three different days, using a Nessler photometric procedure. The samples were dissolved in 20 milliliters 1 to 1, 48 percent HF and up to 15 milliliters 30 percent H_2O_2 . The H_2O_2 was added 5 milliliters at a time at 45- to 60-minute intervals. Dissolution was carried out in polyethylene or platinum beakers covered with a sheet of Teflon by heating on a water bath at about $50^{\circ}C$ for $2\frac{1}{2}$ to 4 hours. Calibration was done by carrying NH_4Cl through the procedure. As usual, intralaboratory agreement was much better than agreement among different laboratories. Chase stated that great care had been taken to insure that the material used was reasonably homogeneous so the differences must have been due to variations in procedure and techniques.

In round-robin 1, only one contributor reported nitrogen results on MAB T-111 by vacuum fusion. They were 9.2, 9.2, and 10 ppm nitrogen. The results were obtained with a 0.2-gram sample, subjected to a 20-minute extraction and platinum bath at $1900^{\circ}C$.

We can only speculate that the reason for the discrepancy between our results of 8 to 10 ppm and Kallmann's Kjeldahl results of about 28 ppm nitrogen (ref. 3) in MAB T-111 is nonhomogeneity. A similar dissolution was used in both cases.

Control of the dissolution and blank determination appear to be the critical steps of the Kjeldahl procedure. Once a sample is in solution, the isolation and measurement of nitrogen can be done very easily and accurately.

CONCLUDING REMARKS

The analytical and precision data reported here evaluate and document the applicability of the vacuum fusion technique for the determination of nitrogen in the tantalum alloys T-111 and T-222. That the vacuum fusion nitrogen values were obtained simultaneously with the determination of oxygen and have an accuracy and precision equivalent to Kjeldahl values is of great importance. Vacuum fusion conditions can be accurately reproduced; the blank is very low and constant; both sample and time are conserved; the oxygen and nitrogen values are related to each other; and no calibration or standards are necessary.

The Kjeldahl results depend on the laboratory atmosphere and thus may be higher or lower in different locations and at different times in the same location. The modified Kjeldahl apparatus and procedure described here have several advantages over usual

Kjeldahl practice for the determination of nitrogen in refractory metals. The use of a 300-milliliter flask with O-ring joint accommodates the large amounts of salts formed and greatly facilitates cleaning after contact with boiling caustic solutions. An inert flushing gas such as argon is more easily controlled than steam distillation. It is also faster as it is unnecessary to heat a large volume of water and there is no contribution to the blank. The high sensitivity obtainable using the nitroprusside-catalyzed indophenol reaction for the spectrophotometric measurement of ammonia nitrogen permits the use of relatively small (1 to 2 g) samples and the precise determination of 10 ppm nitrogen in tantalum alloys.

Since Kallmann's dissolution procedure is applicable to niobium, molybdenum, and tungsten as well as tantalum, it should now be possible to reexamine the determination of nitrogen in many of the refractory alloys of these metals by comparison of vacuum-fusion and Kjeldahl results. It is felt that vacuum-fusion results, which previously have been suspected of being too low, may prove to be more nearly correct than earlier Kjeldahl values, which may have been in error because of inaccurate blank values.

Lewis Research Center,
National Aeronautical and Space Administration,
Cleveland, Ohio, April 23, 1970,
129-03.

APPENDIX A

VACUUM FUSION PROCEDURE

Apparatus and Materials

The vacuum fusion apparatus used in this comparison is described in detail in reference 26. All temperature measurements were made with an optical pyrometer.

Platinum for the bath and flux was prepared by cutting 12-gage wire into uniform 1-gram pieces. Tin was added to the bath as 6- by 6-millimeter pellets weighing about 1.3 grams each.

Sample Preparation

Vacuum fusion samples were cut from T-111 and T-222 rods with a water-cooled abrasive wheel. Burrs were cleaned from the edges of each section with a file. The samples to be analyzed were cut from these sections on a hand operated, flat shear.

Normally, samples for gas analysis by vacuum fusion are cleaned by filing. This method is tedious with small or irregularly shaped samples. For this comparison, acid etching was chosen over filing because it is easier to reproduce a uniformly clean surface without the danger of imbedding foreign material in the sample and because it is similar to the treatment given the samples used for the Kjeldahl method. The vacuum fusion samples were etched for 10 minutes in an equal mixture of 48 percent HF and distilled water heated on a steam bath. Following a distilled water rinse, the samples were dried and rinsed in reagent grade ethyl ether before weighing. The final weight of the vacuum fusion samples ranged from 0.5 to 1.0 gram.

Preparation of Fusion Bath

After the crucible was outgassed at 2400°C for about 2 hours, it was allowed to cool to less than 1600°C . The platinum for the bath was then added to the crucible. The tin was added next allowing a few seconds for each piece to react before dropping the next one. The power on the induction furnace was then reset to give a temperature of $2000^{\circ}\pm 50^{\circ}\text{C}$ in the crucible. Finally, a 0.3- to 0.5-gram piece of T-111 was added to condition the bath, and the bath was outgassed for about 1 hour.

Analysis of Samples

Each sample was added to the crucible along with a 1-gram piece of platinum wire. No attempt was made to maintain intimate contact of sample and platinum at the moment of addition to the bath. The extraction time for samples and blanks was 20 minutes. Outgassing progress was monitored with a liquid-nitrogen-trapped ionization gage attached to the furnace.

Initial composition of the bath was 80 platinum, to 20 tin, exclusive of conditioner. The final composition ranged from 8.7 to 10 parts bath plus flux to 1 part sample. No additional tin was added to the crucible once the bath had been prepared for each day. A typical furnace loading consisted of two 30-gram portions of platinum wire and two 7.8-gram portions of tin for the bath. Twelve samples and 1 platinum wire for each sample plus 2 or 3 for blanks completed the load.

In a single day, 1 blank plus 6 samples with their fluxes were analyzed. At the end of the day, the second portion of platinum and tin bath was added to the crucible and outgassed for about 30 minutes. Two to four replicate analyses were made for each sample rod on at least 3 different days. The blank, nitrogen from the bath plus 1 platinum wire, ranged from 3.9 to 15.7 percent of the total nitrogen measured.

APPENDIX B

KJELDAHL PROCEDURE

Apparatus

The Kjeldahl apparatus (fig. 1): It incorporates a 300-milliliter round bottom flask with an outer 29/42 standard taper joint, sealed by an ethylene-propylene O-ring on the inner joint. A polyethylene diffuser tip with holes made by a No. 53 drill is fashioned from a surgical needle guard. In addition the following were used: spectrophotometer, such as the Beckman Model B, with 1-centimeter absorption cells; narrow-mouth Teflon FEP bottles, 260 milliliters, with tapered solid Teflon stoppers, 6 centimeters long by 2-centimeters in diameter and weighing approximately 25 grams; and polyethylene automatic measuring dispensers.

Reagents

(1) Sodium phenate solution. Add 12 grams phenol to 100 milliliters cold water, then add 7.6 grams $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 5.8 grams NaOH . Stir and add small portions of water until dissolved, finally diluting to 200 milliliters. Prepare as needed and do not chill as the solution is nearly saturated at room temperature.

(2) Sodium nitroprusside solution. Dissolve 25 milligrams $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ in water and dilute to 200 milliliters. Store the solution in the refrigerator and use within 1 hour.

(3) Sodium hypochlorite solution. Dilute 8.0 milliliters commercial bleach (5.25 percent solution of sodium hypochlorite) to 200 milliliters with water and store in the refrigerator. Freshly opened bleach is usually about 0.75 molar in available chlorine as determined by iodometric titration (ref. 1).

(4) Standard nitrogen solution ($1 \text{ ml} \equiv 1 \mu\text{g N}$). Dissolve 3.8193 grams NH_4Cl (dried at 110°C) in water to make 1 liter of stock solution containing 1000 micrograms nitrogen per milliliter. This stock solution is diluted to obtain a standard solution containing 1 microgram nitrogen per milliliter.

(5) Caustic solution (50 percent). Weigh 500 grams NaOH flakes into a stainless-steel, Teflon-lined beaker. Add 600-milliliters distilled water, cover with a ribbed watch glass, and boil for 15 to 20 minutes. Cool quickly in ice water and store in a polyethylene bottle.

(6) Boric acid solution (2.5 percent). Dissolve 25 grams boric acid crystals in water and dilute to 1 liter.

(7) Ammonia-free water. All water used is distilled and then passed through two mixed resin bed demineralizer columns unless indicated otherwise.

(8) Argon gas, 99.998 percent minimum purity.

Analysis of Samples

(1) Cut a 1- to 2-gram piece of tantalum-base alloy sample, preferably from a rod.

(2) Chemically etch the sample by heating it a few minutes in a Teflon beaker with a few milliliters HF and H_3PO_4 and a little K_2CrO_4 . Rinse well with water then with a little acetone, and dry.

(3) Weigh a 1- to 2-gram piece of the metal sample and place it in a 260-milliliter Teflon FEP bottle.

(4) Add 5.0 grams K_2CrO_4 , 50 milliliters 48 percent HF and 5.0 milliliters 85 percent H_3PO_4 to the bottle and loosely insert a solid, tapered Teflon stopper.

(5) Carry two blanks and two standards through the procedure along with the samples. The blanks contain only the reagents. The standards are treated the same as the blanks except that they are spiked with 5 to 20 micrograms nitrogen (added to the flask as a solution of NH_4Cl) just before the distillation.

(6) Boil the samples vigorously on a hot plate for 1 or 2 hours or until dissolved. Any undissolved particles on the bottom can be seen by holding the bottle up to a bright light.

(7) Remove the stoppers and evaporate most of the excess HF, using infrared lamps for additional heating, until salts just begin to precipitate. Move the bottles to a low heat hot plate, and replace the stoppers if the samples are not to be distilled at once.

(8) Remove the stopper from the bottle containing the first sample to be distilled and chill under a stream of cold water.

(9) Transfer the slurry of salts to the distillation flask, rinsing the bottle with portions of water to about 100 milliliters total volume. Before distilling the first sample, purge the distillation apparatus by boiling two 10-milliliter portions of the 50 percent caustic solution in 150 milliliters water for 20 minutes while bubbling 1 liter argon per minute through the solution. After each purge, discard the caustic solution and rinse the flask several times with tap water, dilute HCl, and finally with doubly deionized water before reassembly. The same rinsing procedure is used between each blank, standard, and metal sample.

(10) Connect the flask to the distillation assembly and seal by means of the O-ring joint. Allow the condenser to dip into a receiver containing 5 milliliters 2.5 percent H_3BO_3 and 10 milliliters water. Connect the inert gas line to the gas inlet tube and adjust the flow to 1 liter per minute. As a precaution, the argon is previously bubbled through a gas washing bottle containing 2.5 percent H_3BO_3 solution to remove any impurities which might otherwise be trapped in the distillate and possibly interfere in the color development.

(11) Slowly add 40 milliliters 50 percent caustic solution through the dropping funnel and rinse with 10 milliliters water. The solution will change in color when excess caustic solution is present.

(12) Begin heating the distillation flask. The timer, set for 20 minutes, is started when the spray trap becomes hot to the touch.

(13) About 1 minute before stopping the distillation, lower the receiver so that the condenser tip is above the level of the distillate.

(14) Stop the distillation at 20 minutes, disconnect the flask, discard the salts, rinse the flask, and add the next sample. Transfer the collected distillate, which should total about 50 milliliters, to a 100-milliliter volumetric flask and rinse with a few milliliters of water. The volume is kept to 60 to 65 milliliters.

(15) Store the flasks containing the distillates in a refrigerator until the reagents for the development of the indophenol color are to be added.

Indophenol Color Development and Measurement

(1) To the chilled distillates in 100-milliliter volumetric flasks, add in turn and swirling between each addition 10 milliliters each of sodium phenate, sodium nitroprusside, and sodium hypochlorite reagent solutions. These reagents are conveniently added by means of polyethylene automatic measuring dispensers.

(2) Place the flasks in a water bath at about 40°C , and keep at 30° to 40°C for 30 minutes.

(3) Remove the flasks from the bath, and dilute the solutions nearly to the 100-milliliter mark with water. Then place the flasks for a few minutes in a water bath at 20°C before finally diluting the solutions exactly to the mark.

(4) Mix the solutions well and measure the blue indophenol color in 1-centimeter cells at 630 nanometers against a reagent blank. Beer's law is obeyed and the color is quite stable for 24 hours.

(5) Find the amount of ammonia nitrogen in the sample from a calibration curve. This is prepared by carrying 5- to 30-micrograms nitrogen (added as standard NH_4Cl solution) through the color development procedure and plotting absorbance values against

micrograms of nitrogen added. If the optical density is too large to be read directly, dilute equal aliquots of the sample solution, a reference standard, and the reagent blank with 1 volume of sodium phenate solution and 9 volumes of water. Alternatively, measure the high absorbance sample against a 30-microgram nitrogen per 100-milliliter standard after zeroing the spectrophotometer with the standard solution.

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